

METHODS OF ANALYSIS

CALCULATION OF THE MOLAR VOLUME OF LIQUID ORGANIC OXYGEN COMPOUNDS

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Organic oxygen compounds with long hydrocarbon radicals are used (or can be used as potential feedstock) in production of water- or oil-soluble surfactants, including additives for lube oils and fuels, as well as synthetic oils, plasticizers, and other chemical products. To calculate the chemical-engineering processes for production and conversion of such compounds, it is frequently necessary to know their molar volume. We propose a relatively simple method of determining the molar volume (density) of organic oxygen compounds of different classes: alcohols, alkylphenols, aldehydes, and organic acids, ethers, and esters.

The data for calculating the molar volume of the lower members of homologous series of compounds of different classes are usually available in the literature, but this does not apply to compounds with long alkyl radicals. For this reason, it has been proposed that the molar volume of such compounds be calculated by using the lowest member of the homologous series of compounds of the class examined as the base compound.

It was shown in [1] that the molar volume of liquid hydrocarbons at 20°C can be calculated with the following equation with satisfactory accuracy (maximum error of 5 rel. %):

$$V = V_b + K(N - n) \quad (1)$$

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Table 1

Homologous series	Base compound	Molar volume V_b of base compound, cm ³ /mole	Sum of numbers n of outer electrons
Alcohols	Methanol	40.5	14
Aldehydes	Acetaldehyde	56.3	18
Ketones	Acetone	73.4	24
Ethers	Dimethyl ether	69.7	20
Cellosolves	Ethylene glycol monomethyl ether	78.9	32
Saturated acids	Acetic acid	57.3	24
Saturated acid esters	Methyl formate	61.9	24
Unsaturated acid esters	Methyl methacrylate	73.31	40
Cellosolves	Phenol	78.9	32
Alkyl phenols	Methanol	87.0	36

where V , V_b are the molar volume of the compound sought and the base compound, cm³/mole; $K = 2.696$ is a coefficient treated as the fraction of the molar volume corresponding to a change in the number of outer paraffin radical electrons per unit; N , n are the sum of the number of outer electrons of the compound sought and the base compound; it is determined by summation of the reported numbers of outer electrons at elements C (4), H (1), and O (6).

The molar volumes of the basic compounds in the homologous series of alcohols, aldehydes, ketones, carboxylic acids, alkylphenols, Cellosolves, and saturated and unsaturated carboxylic acid ethers and esters and many outer electrons corresponding to them are reported in Table 1.

The results of calculating the molar volumes of organic oxygen compounds of different classes at 20°C with the proposed equation using the data in Table 1 are reported in Tables 2 and 3.

For most aldehydes, alcohols and saturated carboxylic acids (see Table 2), the agreement of the experimental and calculated values of the molar volumes is satisfactory. However, the proposed equation is not recommended for determining the molar volume of formic acid. The experimental value of its molar volume is 37.7 cm³/mole, while the value calculated with the proposed equation is 41.1 cm³/mole, i.e., the error of the calculation is 9 rel. %, which is greater than the acceptable error of 5 rel. %.

Despite the fact that organic liquids have been investigated for a long time, no acceptable physical theory of the liquid state intermediate between the gas and solid states which could be used a priori to determine their macroproperties has been proposed yet. This could be due to the different directions, including the use of the terms of the theory of physicochemical mechanics of petroleum disperse systems elaborated by the school of Z. I. Syunyaev [2]. According to this theory, the macroproperties of petroleum disperse systems are determined by the intermolecular interactions in them. However, we believe that the macroproperties of any organic liquid can also be determined by the intermolecular interactions.

The lower carboxylic acids have been relatively well investigated [3]. For example, it was found that formic and acetic acids can exist in two forms: *cis* and *trans*. Acetic acid vapors basically contain molecules in the

Table 2

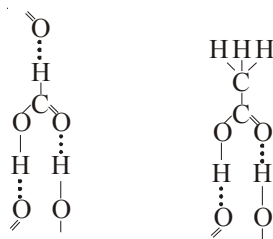
Compound	Number of electrons N	Molar volume V at 20°C, cm³/mole		Error of calculation, rel. %
		experimental value	calculated value	
<i>Aldehydes</i>				
acetic	18	56.3	56.3	0.00
propionic	24	72.0	72.5	-0.70
butyric	30	88.4	88.7	-0.32
valeric	36	106.3	104.8	1.42
capric	42	120.0	121.0	-0.88
enanthic	48	134.0	137.2	-2.35
caprylic	54	156.2	153.4	1.80
pelargonic	60	172.0	169.5	1.43
<i>Alcohols</i>				
Methanol	14	40.5	40.5	0.00
Ethanol	20	58.4	56.7	2.90
<i>n</i> -Propanol	26	74.8	72.9	2.60
<i>n</i> -Butanol	32	91.5	89.0	2.73
1-Pentanol	38	108.2	105.2	2.81
1-Hexanol	44	124.6	121.4	2.59
1-Heptanol	50	141.4	137.6	2.70
1-Octanol	56	157.5	153.7	2.38
1-Nonanol	62	173.8	169.9	2.24
1-Decanol	68	190.9	186.1	2.54
<i>Saturated carboxylic acids</i>				
acetic	24	57.2	57.3	-0.11
propionic	30	74.7	73.5	1.61
butyric	36	91.9	89.7	2.42
valeric	42	108.4	105.8	2.39
capric	48	126.0	122.0	3.16
enanthic	54	141.8	138.2	2.57
caprylic	60	158.7	154.4	2.71
lauric	66	175.9	170.5	2.36

cis form, in which they are more stable. These molecules form nonpolar ring dimers in the vapor phase by hydrogen bonds.

The *trans* form of acetic acid, characterized by a higher dipole moment in comparison to the *cis* form, is more stable in the liquid phase. Based on the calculations of the intermolecular distances in [2, 3], it was concluded

Compound	Number of electrons N	Molar volume V at 20°C, cm ³ /mole	Error of calculation, rel. %	Compound
Ethers				
dimethyl	20	69.73	69.73	0.00
ethyl methyl	26	86.22	85.91	0.37
diethyl	32	103.84	102.08	1.70
dipropyl	44	138.83	134.43	3.17
diisopropyl	44	139.02	134.43	3.30
butyl methyl	38	118.48	118.26	0.19
butyl ethyl	44	135.88	134.43	1.06
dibutyl	56	169.04	166.79	1.34
diisobutyl	56	167.63	166.79	0.50
dipentyl	68	204.50	199.14	2.62
diisopentyl	68	203.71	199.14	2.25
Alkylphenols				
Phenol	36	87.0	87.0	0.00
4-Methylphenol	42	102.8	103.2	-0.41
4-Ethylphenol	48	120.8	119.4	1.23
4-Propylphenol	54	135.0	135.5	-0.41
4-Butylphenol	60	146.1	151.7	-3.80
4-Amylphenol	66	170.7	167.9	1.67
2- <i>tert</i> -Octylphenol	84	217.8	216.4	0.62
4- <i>tert</i> -Nonylphenol	90	233.2	232.6	0.28
4- <i>tert</i> -C ₁₂ -phenol	108	276.9	281.1	-1.52
4- <i>sec</i> -Octylphenol	84	220.2	216.4	1.70
4- <i>sec</i> -Nonylphenol	90	234.4	232.6	0.76
4- <i>sec</i> -Decylphenol	96	248.6	248.8	-0.06
4- <i>sec</i> -C ₁₂ -phenol	108	277.9	281.1	-1.17
4- <i>sec</i> -C ₁₈ -phenol	144	362.5	378.2	-4.33

that the molecules of formic and acetic acids in the liquid state are associated in the form of open chains and that their fixed molecule reacts with two neighboring molecules by hydrogen bonds:



Compound	Number of electrons N	Molar volume V at 20°C, cm ³ /mole	Error of calculation, rel. %	Compound
<i>Esters</i>				
Formic acid esters				
methyl	24	61.9	61.9	0.00
ethyl	30	80.8	78.1	3.38
propyl	36	97.5	94.3	3.31
<i>n</i> -butyl	42	115.0	110.4	3.94
amyl	48	131.2	126.6	3.51
hexyl	56	147.7	148.2	-0.30
heptyl	62	164.2	164.3	-0.10
octyl	68	181.0	180.5	0.25
<i>sec</i> -butyl	42	115.5	110.4	4.36
isobutyl	42	115.4	110.4	4.27
Carboxylic acid methyl esters				
acetic	30	79.4	78.1	1.7
propionic	36	96.3	94.3	2.1
butyric	42	114.2	110.5	3.2
valeric	48	131.3	126.7	3.6
capric	90	246.3	240.0	2.6
Valeric acid butyl ester	66	181.6	175.1	3.6
Capric acid propyl ester	66	182.4	175.1	4.0
Methacrylic acid esters				
methyl	40	73.31	73.31	0.00
ethyl	46	91.68	89.486	2.39
<i>n</i> - propyl	52	107.74	105.662	1.93
isopropyl	52	109.19	105.662	3.23
isoamyl	64	136.37	138.014	-1.20
<i>n</i> -octyl	76	164.96	170.366	-3.28
<i>n</i> -nonyl	82	181.45	186.542	-2.80
<i>n</i> -decyl	88	197.62	202.718	-2.58

The greater associativity (“packing”) and consequently the density of molecules of formic acid in comparison to acetic acid is probably due to differences in the character of the intermolecular interaction in these acids in the liquid state, namely, the reaction of the molecules of formic acid with respect to the C–H group. In our opinion, this can be explained by the difference in the physicochemical properties of these acids within the framework of the theory of donor-acceptor interaction.

According to this theory, some substances (water, alcohols, etc.) are highly structured solvents. It is believed [4] that substances with an acceptor number (AN) greater than 25 can be such solvents. We can

Table 3

R in ROCH ₂ CH ₂ OH molecule	Number of electrons N	Molar volume V at 20°C, cm ³ /mole		Error of calculation, rel. %
		experimental value	calculated value	
CH ₃	32	78.9	78.9	0.00
C ₂ H ₅	38	96.8	95.1	1.77
<i>iso</i> -C ₃ H ₇	44	115.3	111.2	3.54
<i>n</i> -C ₄ H ₉	50	126.8	127.4	-0.53
<i>iso</i> -C ₄ H ₉	50	128.3	127.4	0.67
<i>n</i> -C ₆ H ₁₃	62	147.9	159.8	-8.03
C ₆ H ₅	54	134.1	138.2	-3.03
(C ₂ H ₅) ₂ CHCH ₂	62	163.3	159.8	2.16

Table 4

Compound	Number of electrons N	Molar volume V_b at t_b , cm ³ /mole		Error of calculation with the equation proposed in [1], rel. %
		with the Le Bas method	with the equation proposed in [1]	
<i>Alcohols</i>				
Methanol	14	42.0	42.0	0.00
Ethanol	20	64.2	64.2	0.00
Propanol	26	86.4	86.4	0.00
Butanol	32	108.6	108.6	0.00
Pentanol	38	130.8	130.8	0.00
1-Hexanol	44	153.0	152.9	0.04
1-Heptanol	50	175.2	175.1	0.04
1-Octanol	56	197.4	197.3	0.04
Nonanol	62	219.6	219.5	0.04
1-Decanol	68	241.8	241.7	0.04
<i>Organic acids</i>				
Acetic	24	63.8	63.8	0.00
Propionic	30	86.0	86.0	0.00
Butyric	36	108.2	108.2	0.00
Pentanoic	42	130.4	130.4	0.00
Hexanoic	48	152.6	152.6	0.00
Heptanoic	54	174.8	174.7	0.03
Octanoic	60	197.0	196.9	0.04
Nonanoic	66	219.2	219.1	0.04

hypothesize that the higher the AN of a substance, the higher the degree of its structuring. The AN of formic acid is higher than the number for acetic acid (83.6 versus 52.9), which perhaps is indirect evidence of the greater

structuring of formic acid.

In addition, the singularity of the C–H group in the formic acid molecule is indirectly confirmed by its chemical activity, for example, the ability to be easily added to short bonds in olefin molecules. In view of all of the above, we can hypothesize that association probably takes place in formic acid not only at the carboxyl but also at the C–H group. This also causes much closer packing of the molecules of this acid and its anomalously high density and consequently its lower molar volume in comparison to the values calculated with the proposed equation.

Phenol is a crystalline product at 20°C. For this reason, the calculated value of its molar volume at this temperature should be considered as the molar volume of a liquid in a supercooled state. Phenol is a dimeric formation and remains such a formation, for example, in not very dilute solutions of hydrocarbons.

In calculating the molar volumes of organic acid esters, formic acid methyl ester was used as the base compound. The results of the calculations are satisfactory (the error does not exceed 5 rel. %) when the length of the hydrocarbon radical of both acid and alcohol increases.

Cellosolves are compounds whose molecules have two oxygen atoms in different functional groups: one in a hydroxyl and the other in an ether group. The results of calculations of their molar volumes using the data in [5, 6] are reported in Table 3. The differences from the experimental data are totally acceptable.

An exception is the calculated value of the molar volume of hexyl cellosolve, as the difference is greater than 5 rel. %. The calculation for this compound with the Brettschneider method [7] also does not produce satisfactory results: the error is greater than 5 rel. %.

The molar volumes V_b of the examined compounds at the boiling point t_b calculated with the equation proposed in [1] are reported in Table 4 in comparison to the values calculated with the Le Bas method. There are usually no data on the increment for the oxygen atom in alcohols in many Le Bas increments. We calculated the value of this increment at 12.5 cm³/mole.

The accuracy of the calculations with the proposed equation almost does not differ from the accuracy of the calculations with the Le Bas method.

It follows from the data reported here that the molar volumes of many homologous series of different organic oxygen compounds at both 20°C and at the boiling points can be calculated with acceptable accuracy (maximum error of 5 rel. %) with the relatively simple equations proposed based on knowledge of the empirical formula of the compound sought alone.

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